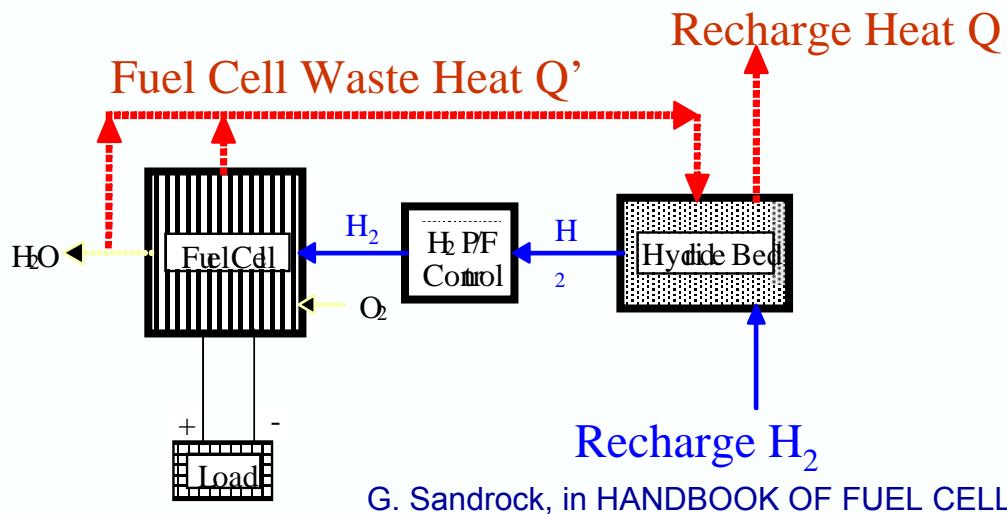


Hydrogen Storage

J. Graetz, J.J. Reilly, J. R. Johnson, J. Wegrzyn, G. Sandrock



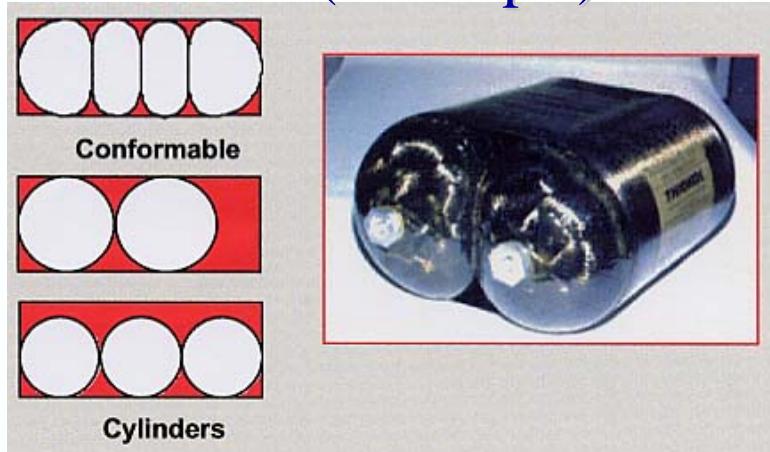
G. Sandrock, in HANDBOOK OF FUEL CELLS, 2003

Liquid (-253° C)



NASA

Gas (5-10 kpsi)



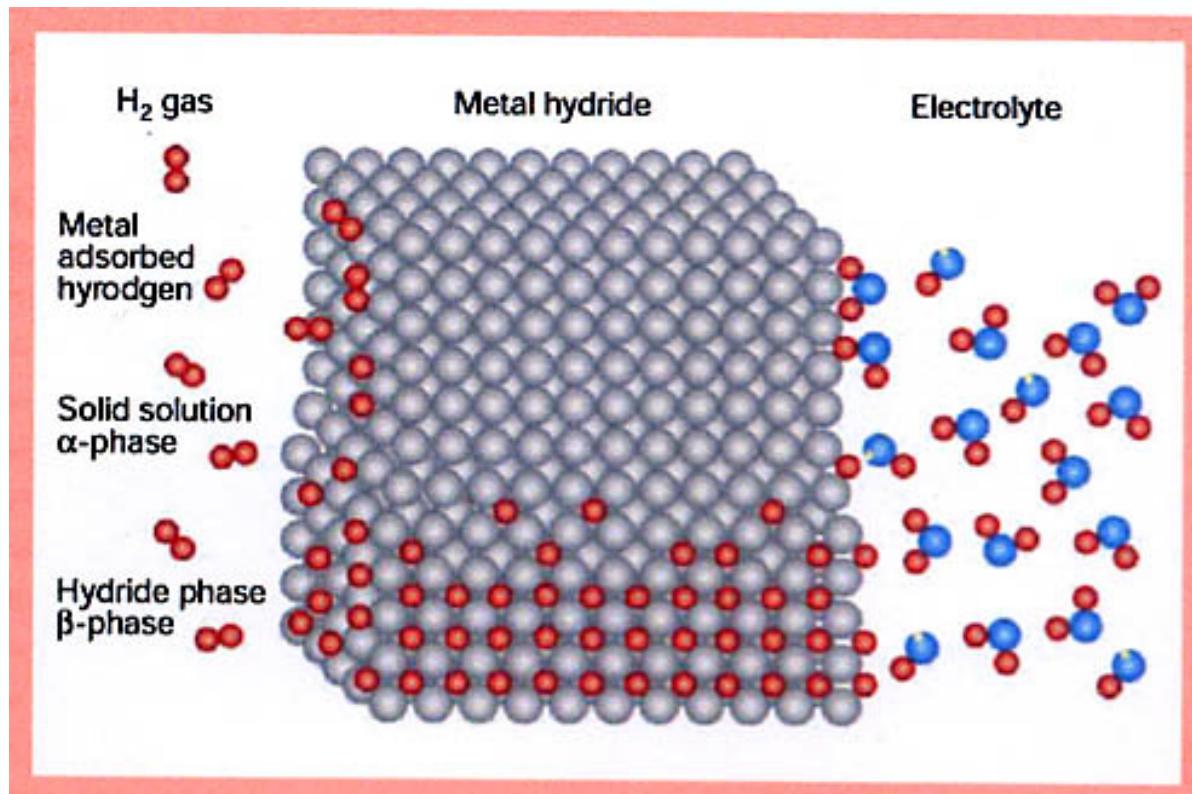
Quantum Technologies

Solid

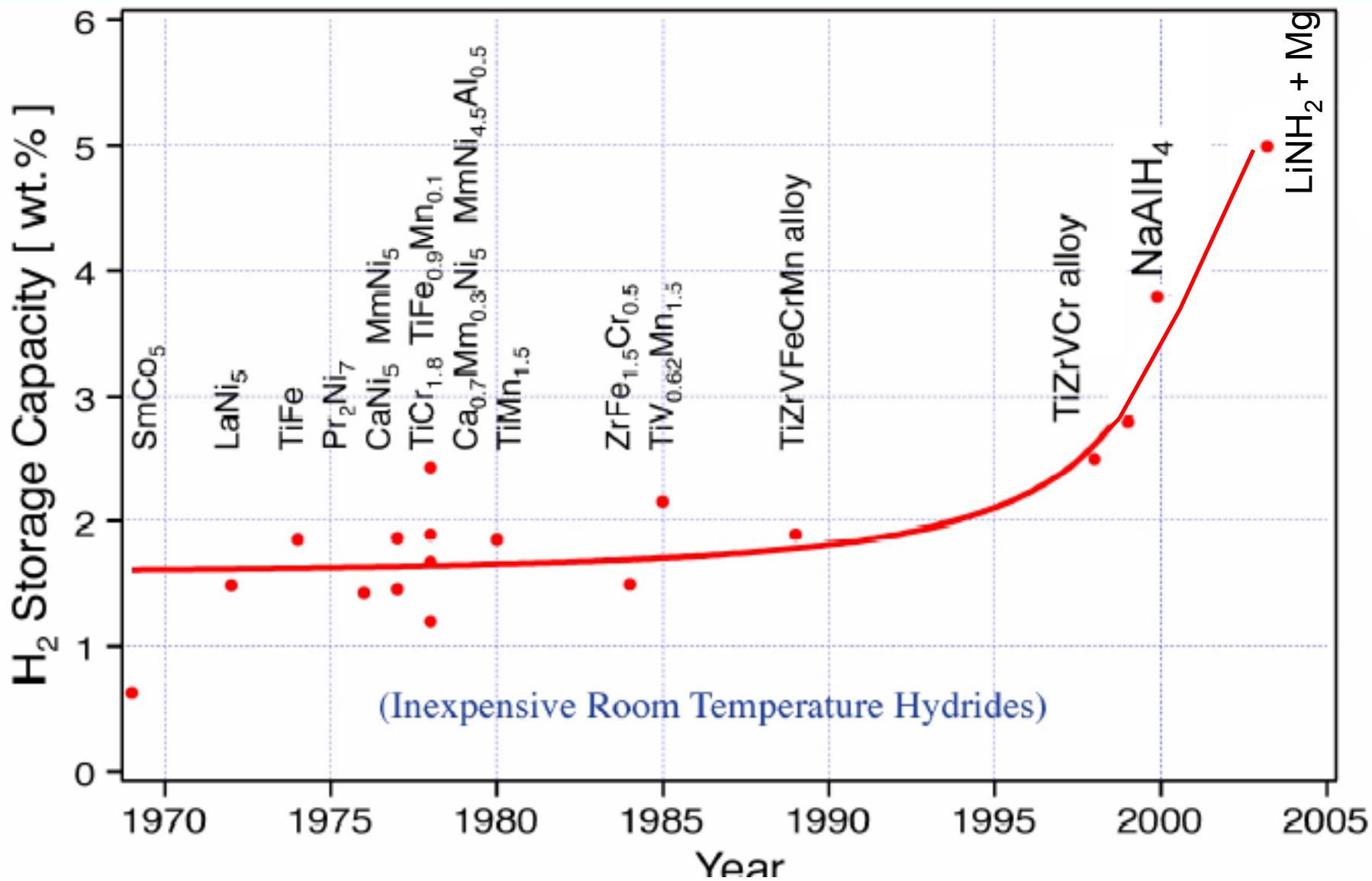


Hydriding Reactions

- Electrochemical: $M+xH_2O+xe^- \leftrightarrow MH_x+xOH^-$
- Gas Phase: $M + x/2H_2 \leftrightarrow MH_x + \text{heat}$



Progress in Reversible H₂ Storage



Alanates

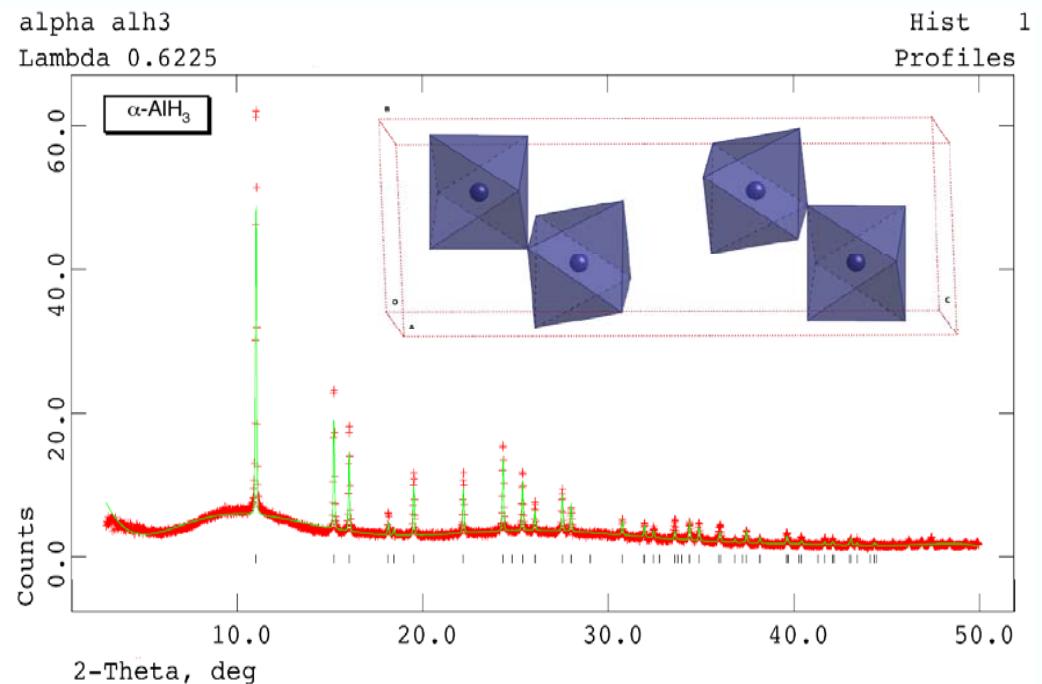
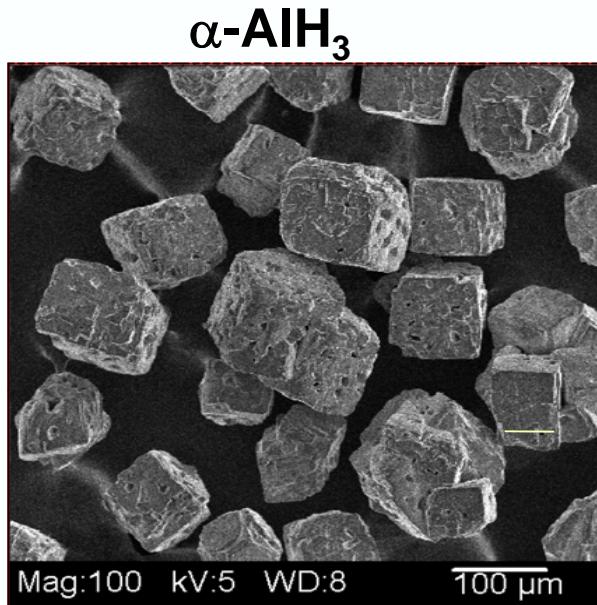


- **What is the mechanism behind reversibility of M-doped Na alanate?**
 - **Surface Catalyst (M^0)**: M acts on surface increasing kinetics but not changing bulk thermodynamics
 - **Substitution (M^{3+} - M^{4+})**: inserting M into lattice will alter bulk thermodynamics and may introduce vacancies*
- **X-Ray Absorption Spectroscopy ideally suited to this problem**
 - valence, density of states, coordination number, interatomic distance
 - long-range order not necessary
 - sensitive at low dopant levels <1 mol%
- Most alanates are either too stable (evolve H_2 at high T) or too unstable (unamenable to rehydriding at moderate P) for automotive applications (w/ PEM fuel cell)
- Thermodynamic tuning - substitution of alkali and other metals to form mixed alanates
- Mixed Alanates:
 - $(\text{M}, \text{M}')^{3+}(\text{AlH}_6)^{3-}$ such as $\text{Na}_2\text{LiAlH}_6$
 - $(\text{M}, \text{M}')^{n+}(\text{AlH}_4)_n$ such as $\text{Na}_{1/2}\text{Li}_{1/2}\text{AlH}_4$

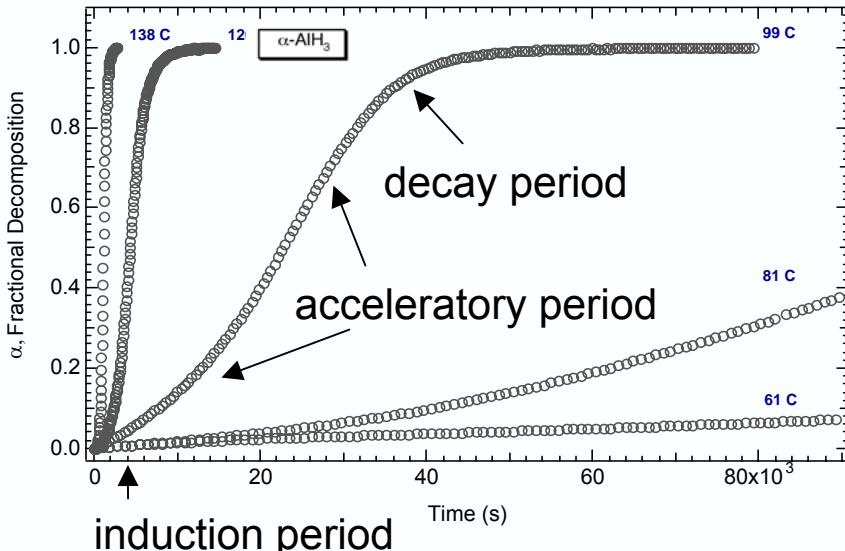
*

Aluminum Hydride AlH_3

- 7 known polymorphs of AlH_3 including: α , α' , β , δ , ε , γ and ζ
- Decomposition: $\alpha\text{-AlH}_3 \rightarrow \text{Al} + 3/2 \text{ H}_2$
- H-capacity (g) = 10.1 wt% (DOE 2010 S-Target = 6.0) > than LH!
- H-capacity (v) = 149 kg/m³ (DOE 2010 S-Target = 45) > than LH!
- $\Delta H_{\text{des}} = 7.6 \text{ kJ/mol H}_2$ (only 20% of NaAlH_4)

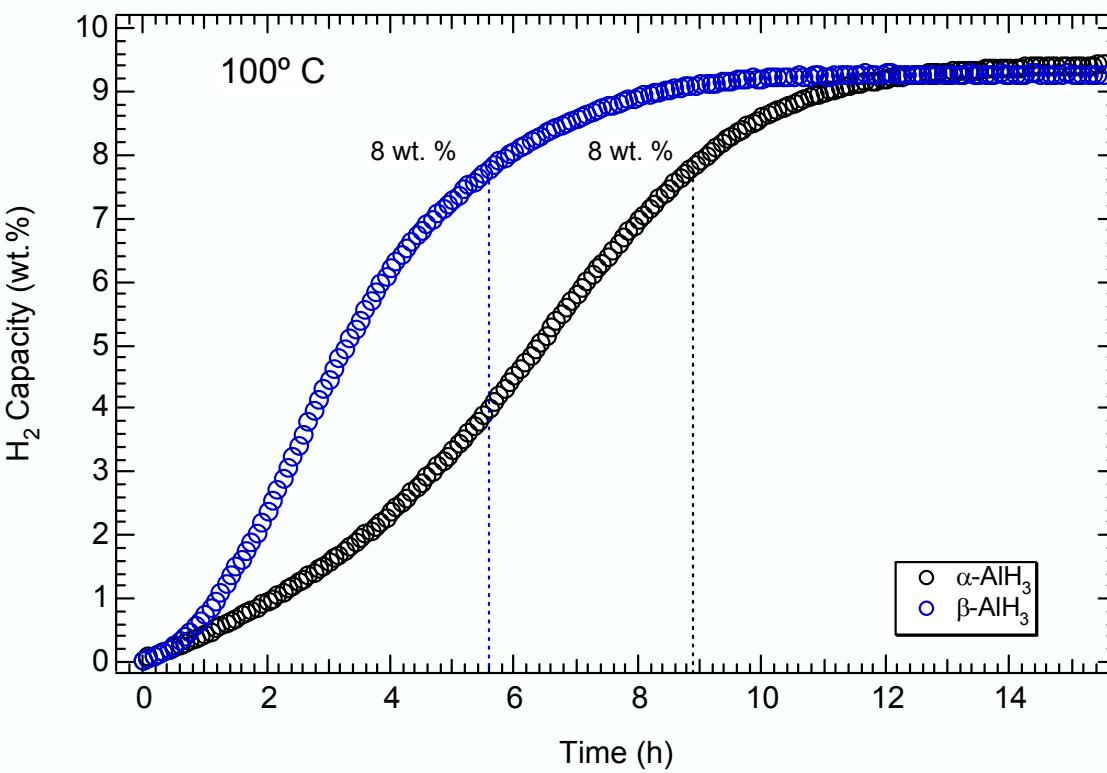


- **Synthesis**
 - $\alpha\text{-AlH}_3$, $\beta\text{-AlH}_3$ and $\gamma\text{-AlH}_3$ prepared by organometallic synthesis
 - H capacities ~ 9.5 wt.%
- **Thermodynamics**
 - Decomposition enthalpy 8-10 kJ/mol
- **Kinetics**
 - Isothermal decomposition curves exhibit a slow induction period followed by an acceleratory period and ultimately a decay period
 - kinetics governed by nucleation & growth of new Al phase



Synthesis Lab	Polymorph	E_a (kJ/mol)	$\ln(A)$
DOW (100 μm crystallites)	$\alpha\text{-AlH}_3^*$	150.3 ± 10.0	38.1 ± 2.5
BNL	$\alpha\text{-AlH}_3$	98.5 ± 2.5	21.9 ± 0.8
BNL	$\beta\text{-AlH}_3$	90.7 ± 8.6	20.1 ± 2.8
BNL	$\gamma\text{-AlH}_3$	74.8 ± 4.3	14.3 ± 1.4

* P. J. Herley, O. Christofferson and R. Irwin, *J. Phys. Chem.* **85** 1887 (1981).



- Chemical Hydrides: $\text{LiBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_3\text{BO}_3 + 4\text{H}_2$
 - 8.6 wt.% (no heat required)
 - Energetically costly regeneration
- Metal Hydrides: $\text{NaAlH}_4 \rightarrow \text{NaH} + \text{Al} + 3/2\text{H}_2$
 - 5.6 wt.% with suitable kinetics at T > 150° C (doped alanate)
 - Reversible on board
- Aluminum Hydride: $\text{AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$
 - 9.5 wt.% (actual) with suitable kinetics at T ~ 100° C (no catalysts/dopants)
 - Reversible @ 28 kbar / Chemical regeneration